Polydopamine-assisted carbon nanotubes/Co$_3$O$_4$ composites for rechargeable Li-air batteries

Taek Han Yoon, Yong Joon Park*

Department of Advanced Materials Engineering, Kyonggi University, Gyeonggi-do 443-760, Republic of Korea

HIGHLIGHTS

► Polydopamine layer was introduced as reacting assistant between the CNTs and the oxide catalyst (Co$_3$O$_4$).
► The polydopamine layer was found to be very effective for the adhesion of nanosized Co$_3$O$_4$ particles on the surface of CNTs.
► The air electrode containing polydopamine-assisted CNTs/Co$_3$O$_4$ composites showed superior catalytic activities in Li-air cells.

ARTICLE INFO

ABSTRACT

We synthesize a carbon nanotubes (CNTs)/Co$_3$O$_4$ nanocomposite and demonstrate its electrochemical properties as an effective catalyst in Li-air cells. In particular, we introduce polydopamine as a binding agent (or reaction assistant) for CNTs and a catalyst with redox properties (Co$_3$O$_4$). Polydopamine coated on the surface of CNTs is expected to offer hydrophilicity and reactivity with oxide-sources. The CNTs/Co$_3$O$_4$ composite prepared using polydopamine layers shows homogeneously dispersed Co$_3$O$_4$ nanoparticles on the surface of the CNTs, thereby confirming that our new facile approach allows effective interaction between the carbon support and the oxide component. The air electrode containing polydopamine-assisted CNTs/Co$_3$O$_4$ composites shows superior catalytic activities in Li-air cells. This can be attributed to the wide catalytic-active area that provides well-dispersed nanosized Co$_3$O$_4$ particles as well as to the reduced contact resistance as a result of the close contact between CNTs and oxide (Co$_3$O$_4$).

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1. Introduction

Li-air batteries are one of the most promising new technologies among the various energy storage systems owing to their extremely high theoretical energy density [1–7]. However, the maximum theoretical energy density of Li-air batteries cannot be fully achieved in practice. In the case of Li-air battery systems using non-aqueous (organic) electrolytes, the practically available capacity of the system is highly attributed to the air electrode composed of a catalyst and a carbon material [8–13]. The air electrode significantly affects the rechargeability and overpotential properties of the Li-air cell. Among the components of the air electrode, the catalyst is important in that it can enhance the charge reaction by reducing the voltage required to dissociate the reaction products (such as Li$_2$O$_2$) into lithium metal and oxygen [14]. However, the oxide catalysts, which are generally used for air

electrodes, are poor electric conductors and they are typically used mixed with porous carbon materials for reaction and as storage sites for reaction products. Although some types of carbons show catalytic activity this is not typically sufficient to dissociate the reaction products and produce oxygen evolution [9–12]. Considering separated roles of the catalyst and the carbon material, a composite electrode would be more effective in enhancing the catalytic activity of air electrodes. In particular, if the nanosized catalysts could be homogeneously dispersed on the surface of the porous carbon material, the number of catalytic active sites would be increased, thereby improving the electrochemical activity of the air electrodes.

Herein, a nanosized oxide-catalyst was composited with CNTs to enhance the catalytic activity of the air electrode in Li/air batteries. The methods for preparing these composite electrodes have been reported considerably [15–17]. In this study, a new and facile approach based on the introduction of a polydopamine coating layer as a special adhesive between the carbon and the oxide is described. The polydopamine coating has discovered in the process of analyzing the mussel's special ability. Thus, mussels can be

* Corresponding author.
E-mail addresses: yjpark2006@kyonggi.ac.kr, yjparketri@yahoo.co.kr (Y.J. Park).

strongly attached to all types of organic/inorganic surfaces. The Messersmith group attributed this strong adhesion ability to the presence 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine amino acids [18,19]. Based on this finding, polydopamine containing both DOPA and lysine side chain functionalities was suggested as a strong binding agent. Remarkably, the polydopamine coating layers were found to be a versatile platform for secondary surface-mediated reactions [19]. For example, a polydopamine layer significantly promoted the reaction of various source materials such as metals, ceramics, and polymers with the coated substrates [19–23]. Based on the understanding of this special ability of polydopamine, we used it as a binding agent between carbon and the oxide catalyst. This process is very simple and facile, and is a green technology. Moreover, this method can be applied not only to CNTs but also to any type and shape of carbon materials.

We report herein a new process to fabricate CNTs/Co$_3$O$_4$ composites using a polydopamine layer, and their electrochemical property, as air electrodes for Li/air cells were determined. To the best of our knowledge, this is the first study reporting a polydopamine coating approach in carbon and oxide-containing electrodes. Co$_3$O$_4$ has generated an extensive interest as a promising catalyst in various application fields [24–27]. The CNTs serve to support the catalyst, thereby providing a surface for the redox reaction to occur. It is expected that the CNTs/Co$_3$O$_4$ composite shows excellent catalytic activities because of the nanoscale catalytic size, large surface area for reaction, and enhanced electronic conductivity.

2. Experimental

2.1. Synthesis of polydopamine-assisted CNTs/Co$_3$O$_4$ composite

All the chemicals used herein were of analytical purity and used as received. The polydopamine-coated CNTs material was prepared by simple immersion of the CNTs into a dopamine solution containing a tris-buffer solution (10 mM, pH 8.5) and methanol as co-solvents (CH$_3$OH:buffer = 1:1 v/v). The mixture solution was mechanical stirred for 4 h at room temperatures until a good suspension was formed. After that, the suspension was centrifuged and the solid was subsequently washed with distilled water and ethanol. The polydopamine-coated CNTs were dispersed in 50 ml of a 4 mM Co(NO$_3$)$_2$·6H$_2$O (cobalt nitrate hexahydrate) aqueous solution for 30 min. Subsequently, a 0.2 M NH$_4$OH aqueous solution was slowly dropped into the above solution to adjust the pH value to 10, and then stirred for 8 h. After that, the mixture solution was centrifuged, the resulting solid washed for several times with ethanol and distilled water, and then dried at 90 °C for 24 h. Finally, the dried product was annealed under air at 450 °C for 4 h, after which the final product was obtained. Fig. 1 illustrates the overall fabrication process of polydopamine-assisted CNTs/Co$_3$O$_4$ composites.

The X-ray diffraction (XRD) patterns of the samples were obtained with a Rigaku X-ray diffractometer equipped with monochromatized Cu-Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe (Ulvac-PHI)) analysis was
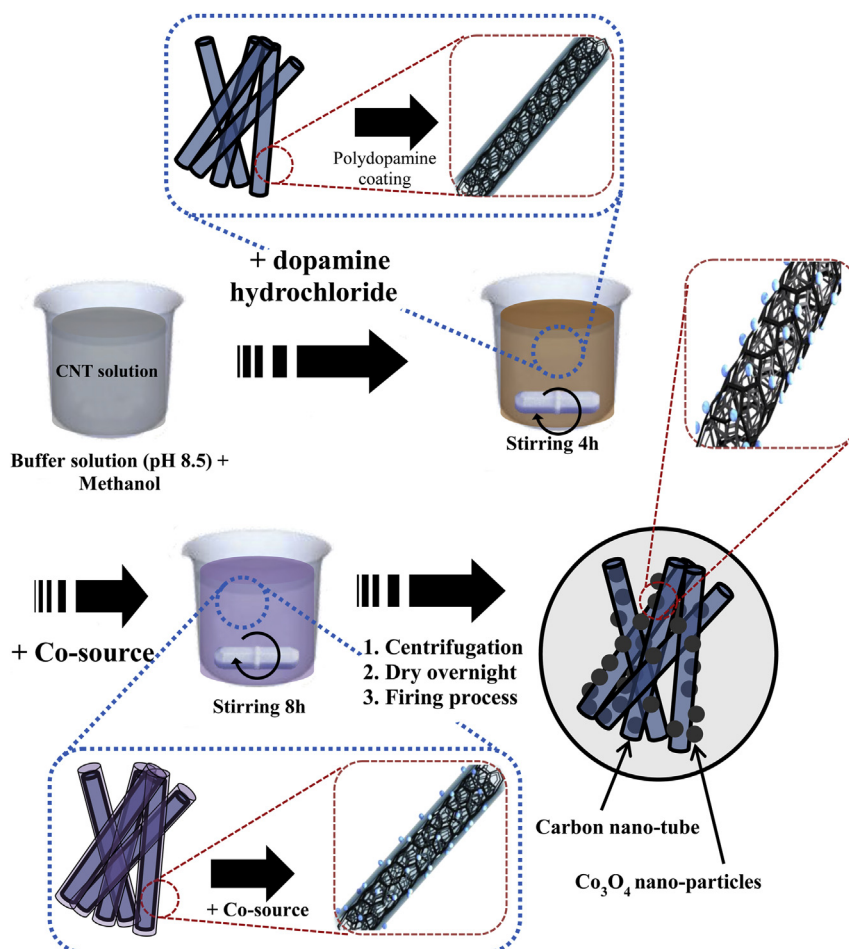

Fig. 1. Scheme of the synthetic procedure for obtaining polydopamine-assisted CNTs/Co$_3$O$_4$ composites.

used to confirm the presence of the dopamine-coating layer on the CNTs. The microstructure of the compound was observed using field-emission scanning electron microscopy (SEM, Hitachi S-4700) and transmission electron microscopy (TEM, AP tech TECNAI G2 F30 S-Twin). The CNTs:Co_3O_4 ratio was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and thermogravimetry (TG, STA S-1500) analyses.

2.2. Measurement of electrochemical property

The electrochemical performance of the air electrode containing a polydopamine-assisted CNTs/Co_3O_4 composite as a catalyst was examined using a modified Swagelok cell consisting of an air electrode, a metallic lithium anode, a glass filter separator (Whatman), and a 1 M LiTFSi in TEGDME (tetraethylene glycol dimethyl ether) electrolyte. The air electrode contained 72 wt% of catalyst (CNTs/Co_3O_4 composite), 18 wt% of carbon (ketjen black) and 10 wt % of binder (PVDF). Since the CNTs:Co_3O_4 ratio in the composite was 72:28, the Co_3O_4 (oxide catalyst) loading of the electrode was ~20 wt%. Air electrodes containing nanosized commercial Co_3O_4 powder (Aldrich, particle size: ~50 nm) were also prepared with the same Co_3O_4:carbon (ketjen black):binder ratio (20:70:10) as standard electrodes for comparing the electrochemical properties of the composite electrode. An electrode containing pure CNTs (72 wt%, 18 wt% of Ketjen black and 10 wt% of binder) as catalyst was also fabricate to characterize the catalytic activity of CNTs. All of the components were ball milled for homogeneous mixing, coated on a carbon paper (JNTC Co.), and dried at 90 °C for 2 h. Several holes were made on one side of the Swagelok cell rod, thereby exposing the air electrode to the atmospheric O_2. The cells were assembled in an Ar-filled glove box and subjected to galvanostatic cycling using a WonAtech (WBCS 3000) charge–discharge system. The experiments were carried out under 1 atm of O_2 in an air chamber. Secondary ion mass spectrometry (SIMS) analysis was applied for the characterization of the air electrode to obtain information about the reaction products on cycling. The CAMECA IMS-6f Magnetic Sector SIMS at the Korea Basic Science Institute (Busan center) was used for the measurement. The phase of the reaction products on cycling was confirmed by HP-XRD (High power X-ray diffraction) analysis.

3. Results and discussion

3.1. Effect of polydopamine coating as a special reaction assistant

With the aim to confirm the formation of the polydopamine coating layer, an XPS analysis was performed. Fig. 2a shows the XPS spectra of the plain CNTs, the polydopamine-coated CNTs, and the polydopamine-assisted CNTs/Co_3O_4 composites. While the plain CNTs exhibited only peak corresponding to C, the polydopamine-coated CNTs exhibited new peaks attributed to N and O. These newly detected peaks are coincident with reported XPS peak of polydopamine [28], which confirms the formation of the polydopamine layer on the surface of the CNTs. The XPS spectra of the polydopamine-assisted CNTs/Co_3O_4 composite clearly showed a new peak corresponding to Co, indicating the existence of cobalt. However, the peak attributed to N was not detected in this case which indicates that the polydopamine layer was removed upon the heat-treatment process. The existence of Co_3O_4 nanoparticles composited with CNTs was also confirmed by an X-ray diffraction (XRD) analysis. The top portion of Fig. 2b shows the diffraction peaks for the polydopamine-assisted CNTs/Co_3O_4 nanocomposite. A broad peak at ~$2\theta = 23.5°$ corresponding to the CNTs was observed along with sharp crystalline peaks. The crystalline peaks were perfectly indexed to a typical Co_3O_4 crystalline
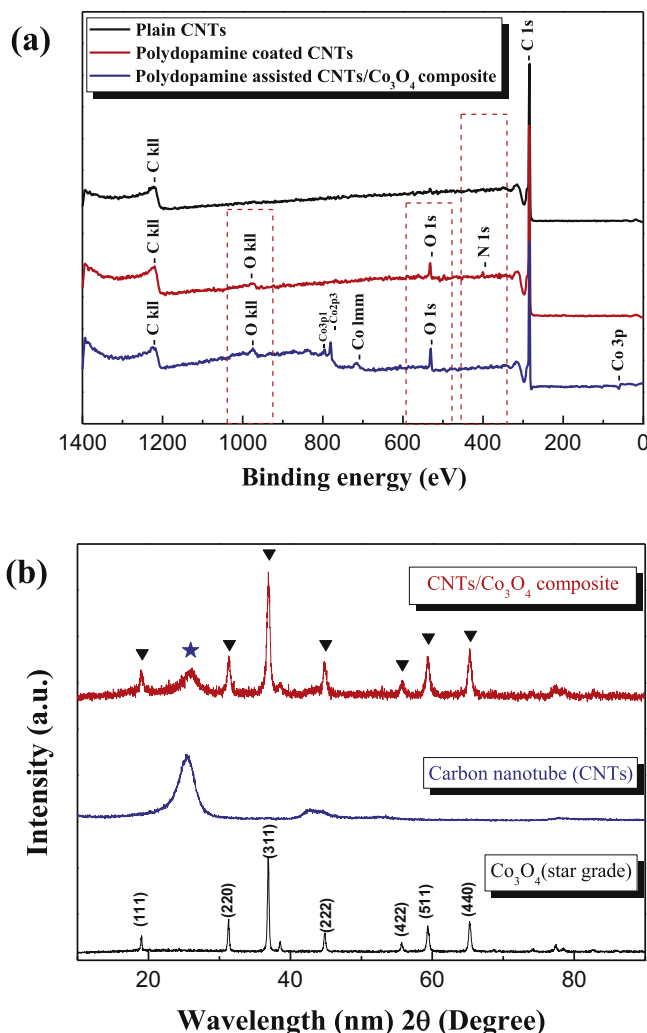
Fig. 2. (a) XPS spectra of pristine CNTs, polydopamine-coated CNTs, and polydopamine-assisted CNTs/Co_3O_4 composites. (b) XRD patterns of CNTs, Co_3O_4 commercial powder, and polydopamine-assisted CNTs/Co_3O_4 composites.

phase with a spinel structure, thereby indicating that a Co_3O_4 crystalline phase was successfully formed upon our new fabrication process.

Fig. 3a–c shows a typical SEM image of a CNTs/Co_3O_4 composite using polydopamine coating. The pictures indicate that the nanosized Co_3O_4 particles were well attached on the surface of the CNTs. With the aim to determine the surface morphology of the polydopamine-assisted CNTs/Co_3O_4 composite in detail, several TEM images were obtained. As shown in Fig. 3d–f, it is clear that the surface of the CNTs was very homogeneously dispersed with Co_3O_4 nanoparticles. The sizes of these nanoparticles were lower than 10–20 nm. The SEM and TEM images confirm that the pre-formed polydopamine coating layer on the surface of CNTs successfully acted as an adhesive between CNTs and Co_3O_4 nanoparticles. Note that except polydopamine coating, the CNTs were not subjected to any treatment for reaction with Co_3O_4 source material. CNTs are typically treated with acid to increase their hydrophilicity and reactivity with oxide-sources in the process of composition. However, the defects formed onto the surface as a result of the acid treatment may deteriorate the conductivity of CNTs. In contrast, our new method does not need acid treatment because polydopamine layer is sufficiently reactive and highly hydrophilic.
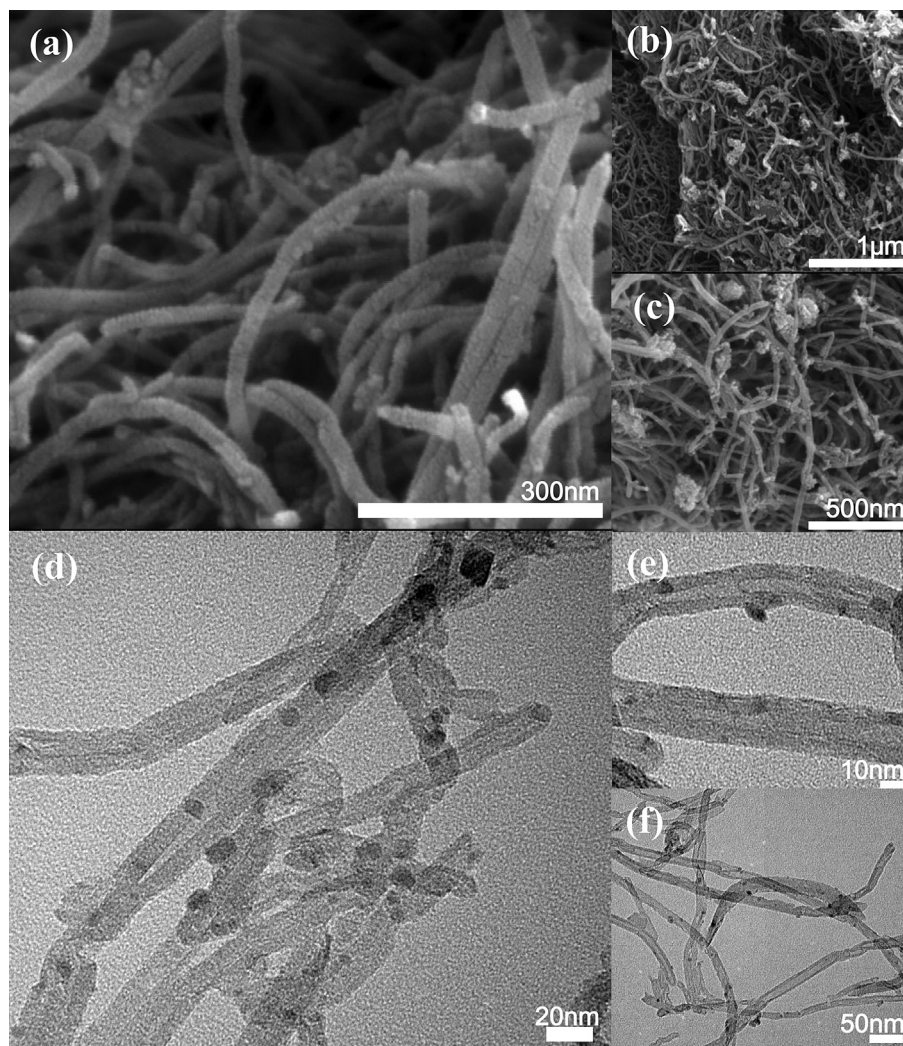
Fig. 3. Images of particles of the polydopamine-assisted CNTs/Co$_3$O$_4$ composite fabricated by the procedure illustrated in Fig. 1. (a)–(c) SEM images; (d)–(F) TEM images.

To confirm the effect of polydopamine layer as an adhesive (or special reaction-assistant), we fabricated CNTs/Co$_3$O$_4$ composites without using polydopamine coating following the same fabrication process explained in Fig. 1. Fig. 4 shows the SEM (Fig. 4a–c) and TEM (Fig. 4d–f) images of the polydopamine-free CNTs/Co$_3$O$_4$ composites. Unlike the polydopamine-assisted material, these composites showed Co$_3$O$_4$ particles with a large size (∼200–300 nm) accumulated on the bundles of CNTs. The oxide particles were severely aggregated. These images suggest that the Co$_3$O$_4$ precursors did not homogeneously react on the surface of CNTs, and they simply aggregated and crystallized upon the heating process. The reactivity between CNTs and Co$_3$O$_4$ can be improved if some methods such as acid treatment are used. However, comparing Figs. 3 and 4, it is clear that the polydopamine layer is a very effective reaction assistant (or binding agent) between CNTs and Co$_3$O$_4$ nanoparticles. This new and facile composition process could be adapted for a variety of carbon materials and oxides for various application fields.

Considering the TG results of the polydopamine-assisted composite, the weight ratio of the CNTs to the Co$_3$O$_4$ crystalline phase was calculated to be 72:28, which was also confirmed by ICP-AES analysis. On the other hand, the CNTs prepared without using polydopamine layer were composed of 50 wt% of Co$_3$O$_4$ as a result of large aggregation.

3.2. Electrochemical properties of polydopamine-assisted CNTs/Co$_3$O$_4$ composites

With the aim to investigate the electrochemical properties of the polydopamine-assisted CNTs/Co$_3$O$_4$ composites in Li-air cells, air electrodes were prepared and tested. A 1 M LiTFSI solution in TEGDME was used as an electrolyte to avoid decomposition of electrolyte upon cycling [29–31]. The selection of an appropriate current collector is an issue for the fabrication of air electrodes. In the common configuration, the air electrode composed of the catalyst and the carbon material is attached to the current collector. Up to now, the majority of Li-air studies have used a Ni form or a Ni mesh as current collectors [8–10]. However, it is reported that Ni clearly promotes the electrochemical degradation at potentials greater than 3.5 V as a result of the reaction between Ni and the electrolyte [32]. In this sense, porous carbon paper such as GDL (gas diffusion layer) could be an alternative to avoid unwanted reactions with the electrolyte. However, the carbon paper itself is suspected to show some catalytic activity, thereby adding some confusion in the analysis of the catalytic properties of the air electrode material. Fig. 5 compares the initial capacity of the air electrode containing the CNTs/Co$_3$O$_4$ composite and the plain carbon paper without electrode material measured at a current density of 0.2 mA and two electrodes with the same area. The capacity, highlighted in small
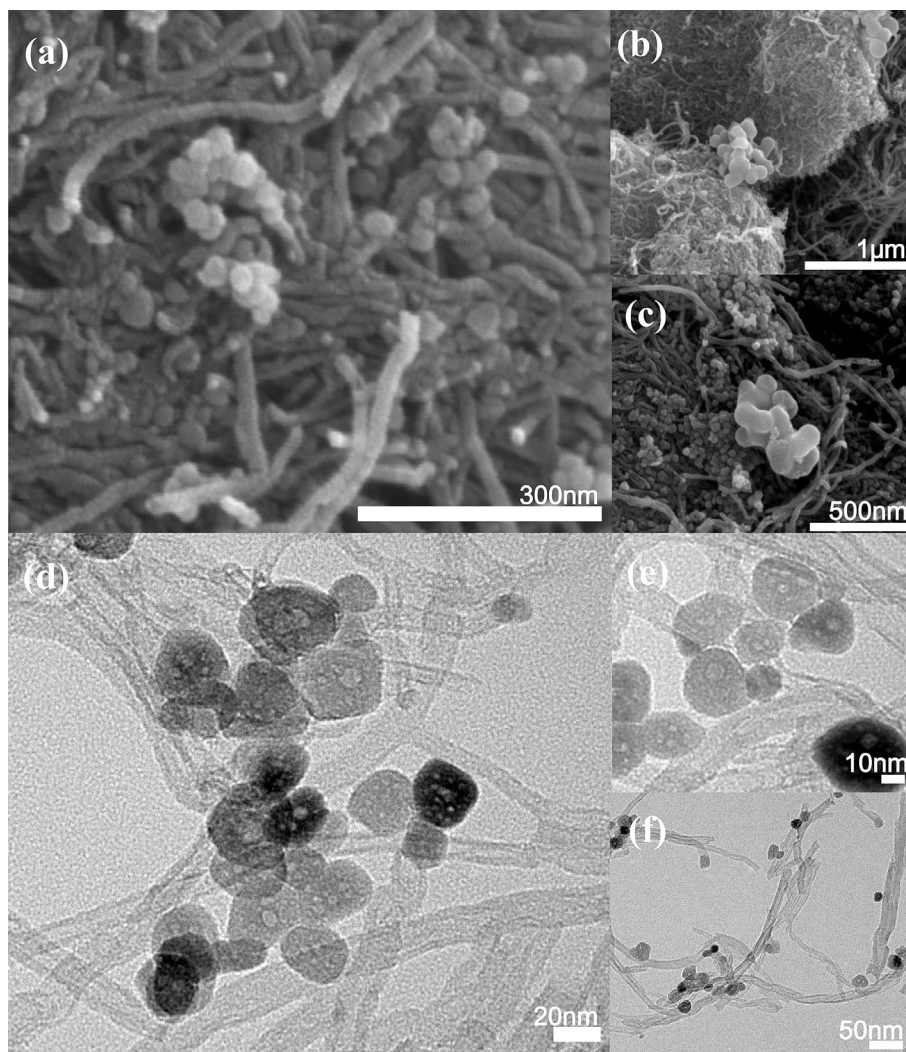
Fig. 4. Images of particles of the CNTs/Co$_3$O$_4$ composite fabricated by the procedure illustrated in Fig. 1 but without dopamine coating process. (a)–(C) SEM images; (d)–(F) TEM images.
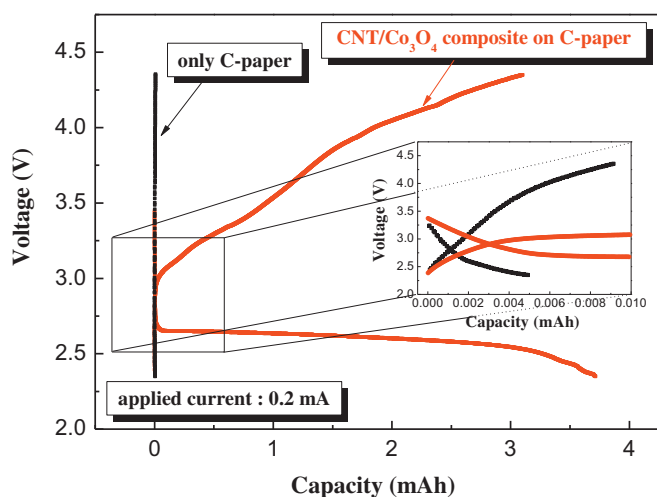

Fig. 5. Comparison of the initial capacity of the air electrodes containing polydopamine-assisted CNTs/Co$_3$O$_4$ composites and plain carbon paper without electrode material measured at a current density of 0.2 mA. A marked "square" is highlighted to present the discharge–charge profile of the plain carbon paper (current collector).

insets, clearly confirmed that the catalytic activity of the plain carbon paper is negligible. Thus, all of the following electrochemical tests of our work were performed using carbon paper as a current collector to avoid the negative effects attributed to Ni.

Fig. 6 shows the initial capacity of the air electrodes containing polydopamine-assisted CNTs/Co$_3$O$_4$ composite as a function of the electrode loading weights and current densities used for the tests. The capacity values reported in this article were based on the total electrode mass (CNTs/Co$_3$O$_4$ composite + carbon + binder), which may be a reasonable approach to present the energy storage ability as rechargeable batteries. Interestingly, the electrochemical performance of the air electrode was highly dependent upon the measurement conditions. As shown in Fig. 6a, the discharge capacity of the composite remarkably changed depending on the electrode material loading weight (composite (catalyst) + carbon + binder). Thus, the electrode with a loading of 1 mg cm^{-2} showed a discharge capacity of ~6300 mAh g$_{electrode}^{-1}$ at a constant current density of 200 mA g^{-1} and voltages in the range 2.35–4.35 V. However, higher electrode loadings (1.8 and 2.4 mg cm^{-2}) showed significantly decreased discharge capacity values (~3000 and ~2200 mAh g$_{electrode}^{-1}$, respectively). This indicates that the simple comparison of the specific capacity of the electrodes containing different loading weights is meaningless. Heavy loading weights may lead to thick electrode layers
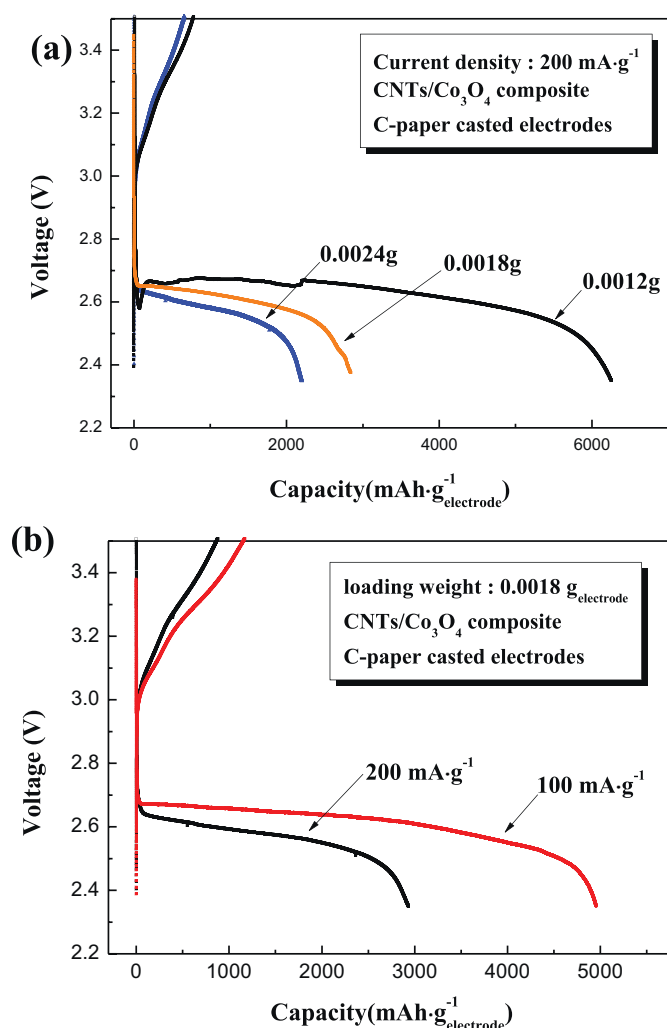
Fig. 6. Initial capacity of the air electrode containing polydopamine-assisted CNTs/Co$_3$O$_4$ composites measured at a variety of: (a) Loading weights of electrode, and (b) current densities for test.

3.3. Comparison of the electrochemical properties of air electrodes

With the aim to compare the electrochemical properties of the polydopamine-assisted CNTs/Co$_3$O$_4$ composite with the rest of prepared materials, two different electrodes were prepared. One (CNTs + ketjen black, KB mixture) was prepared using a mixture of CNTs (72 wt%), carbon (KB, 18 wt%), and binder (10 wt%) was prepared for characterizing the catalytic properties of CNTs. The second electrode was fabricated by simple mixing the commercial plain nanosized Co$_3$O$_4$ powder, the KB, and the binder at the same Co$_3$O$_4$: carbon: binder ratio (20:70:10) with the electrode containing the polydopamine-assisted CNTs/Co$_3$O$_4$ composite material. These two electrodes were considered as standard electrodes to compare the electrochemical properties with that of the composite electrode.

Fig. 7 shows the discharge−charge profiles of the three different electrodes for three initial cycles. (The right side of the figures presented SEM images of the measured electrodes) The voltage range was 2.35−4.35 V and the current density was fixed at 200 mA g^{-1}. The loading weight of the electrodes was adjusted to 1.8 ± 0.1 mg cm^{-2}. As shown in Fig. 7a, the CNTs + KB mixture presented a relatively high discharge capacity ($\sim$5000 mAh g$^{-1}_{\text{electrode}}$). However, this capacity was largely decreased upon cycling, and only $\sim$20% and 10% of the initial discharge capacity remained after the second and third cycle, respectively. The initial discharge capacity of the electrode containing commercial Co$_3$O$_4$ nanopowders was $\sim$2000 mAh g$^{-1}_{\text{electrode}}$ (Fig. 7b), which is considerably lower than that of the electrode containing the CNT + KB mixture. The reversibility of the electrode seemed to be a little improved by using commercial Co$_3$O$_4$ nanopowders, although this enhancement was not significant. In contrast, the initial capacity of the polydopamine-assisted CNTs/Co$_3$O$_4$ composite electrode was $\sim$3000 mAh g$^{-1}_{\text{electrode}}$, which is somewhat higher than that of the electrode containing commercial Co$_3$O$_4$ nanopowders (Fig. 7c). Moreover, the composite-containing electrode showed a largely enhanced reversibility. Thus, over 40% of the initial discharge capacity was maintained after the third cycle in the composite electrode.

The investigation of the over-potential during charging and discharging processes is an effective method to analyze the catalytic activity of the air electrodes. The standard potential of the air cell can be calculated from the free Gibbs energy data. However, the real charging and discharging potentials typically deviate from the standard potential because the electrode reactions are suppressed by the limiting factors, thereby producing the so-called "over-potential." Thus, the over-potential represents the extra energy required to drive the reactions at a specific current density [11]. In particular, high over-potentials are typically obtained because reaction products such as peroxides (Li$_2$O$_2$), formed during the discharge process require large extra energy to be decomposed into lithium ions and oxygen. Fig. 8 compares the over-potential of the initial discharge−charge profiles shown in Fig. 7. The electrodes containing the CNTs + KB mixture and the commercial Co$_3$O$_4$ powder showed high over-potentials (average charge voltage was over 4.0 V). In contrast, the over-potential of the electrode containing the polydopamine-assisted CNTs/Co$_3$O$_4$ composite was largely decreased. In particular, the average charge voltage was significantly decreased to $\sim$3.6 V. This indicates that the polydopamine-assisted CNTs/Co$_3$O$_4$ composite acts as an effective catalyst to decompose reaction products such as Li$_2$O$_2$. Considering the reaction model for an air electrode [11–13], most of the active sites in the electrode may be located at the catalyst/carbon contact area. The general fabrication process of an air electrode involves simple mixing of the catalyst and the carbon material, thereby leading to a nanosized catalyst with a poor dispersion. Thus,
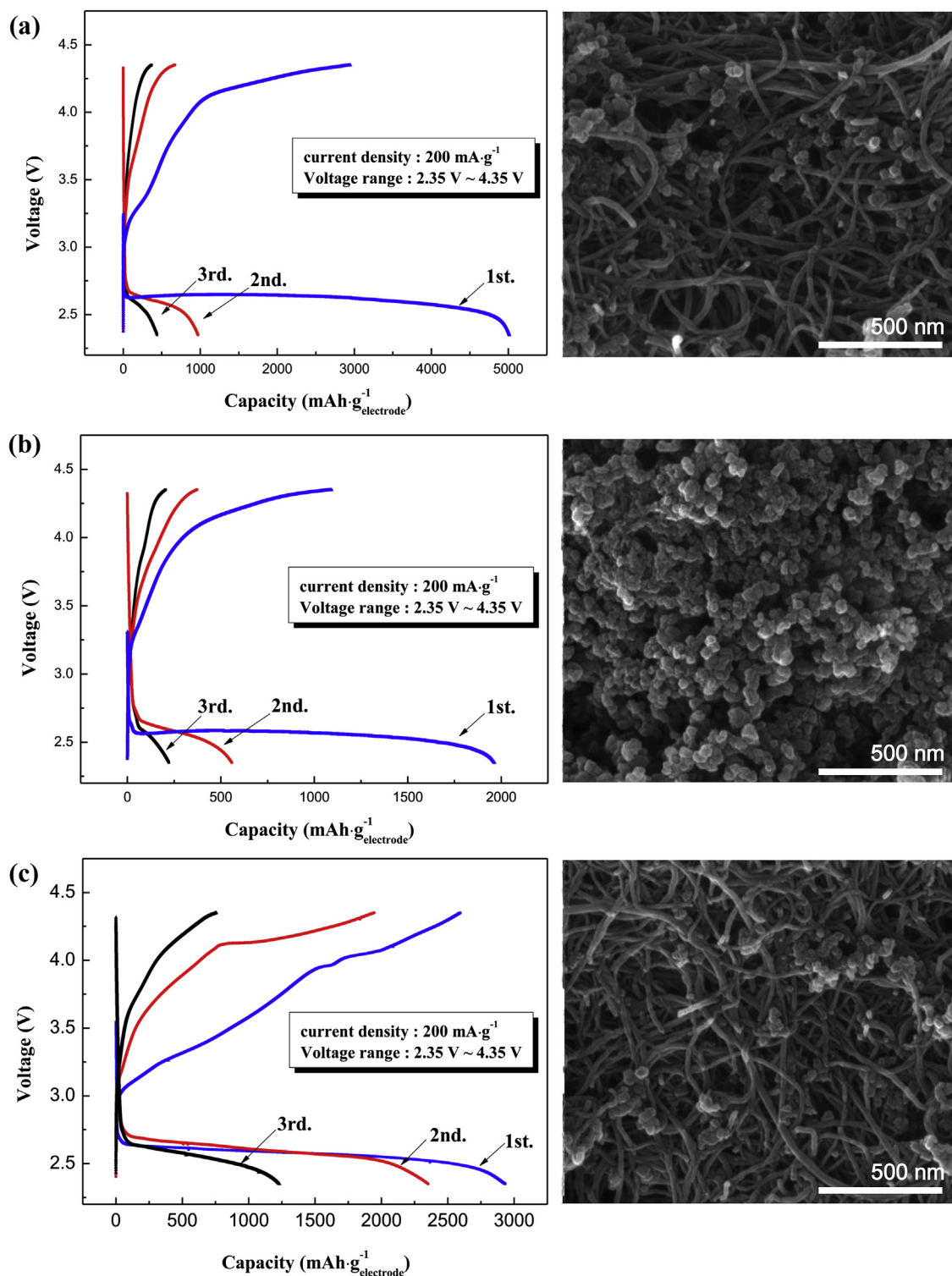
per area of the electrode. However, based on this result, thick electrodes may be detrimental to allow the full catalytic activity of the electrode materials. Consequently, it would favorable to prepare catalyst (+carbon) layer as thin as possible in order to prepare electrodes with high catalytic activities. In our work, we tried to adjust the loading weight of the electrode and the thickness of the (catalyst + carbon) layer to a constant value in order to provide reliable tests.

The specific capacity of the air electrodes was also found to be very sensitive to the current density. Fig. 6b presents the initial discharge−charge profiles of the electrodes containing polydopamine-assisted CNTs/Co$_3$O$_4$ composite (loading weight: 1.8 mg cm^{-2}). While the discharge capacity of the electrode was $\sim$3000 mAh g$^{-1}_{\text{electrode}}$ at a current density of 200 mA g^{-1}, this value was significantly increased ($\sim$5000 mAh g$^{-1}_{\text{electrode}}$) as the current density decreases to 100 mA g^{-1}. In the case of Li-air cells using non-aqueous (organic) electrolytes, reaction products such as solid Li$_2$O$_2$ were formed during the discharge process. A reaction mechanism involving solids may limit the reaction kinetic, thereby leading to relatively low rate capabilities. However, considering that a 1 C rate of the cathode containing LiCoO$_2$ in lithium ion cells is equivalent to approximately 120 mAh g$^{-1}_{\text{electrode}}$, current densities of 100 and 200 mA g^{-1} are reasonable to investigate the commercially available capacity of the air electrode.

Fig. 7. Discharge–charge profiles of the three different electrodes after three initial cycles (The right side of the figures presented SEM images of the measured electrodes): (a) Electrode containing CNTs as a catalyst; (b) Electrode containing commercial Co_3O_4 nanoparticle as a catalyst; (c) Electrode containing polydopamine-assisted CNTs/Co_3O_4 composite as a catalyst (voltage range: 2.35–4.35 V, current density: 200 mA g^{-1}).

partially aggregated catalysts may not fully exhibit their catalytic activity. In contrast, the polydopamine-assisted CNTs/Co_3O_4 composite-containing well-dispersed Co_3O_4 nanoparticles (10–20 nm size) on the surface of CNTs could provide a larger catalyst/carbon contact area leading to a superior catalytic activity. Moreover, the strong interaction between Co_3O_4 catalyst and CNTs could reduce contact resistance and enhance long-term stability.

As displayed in the upper panel of Fig. 8, the capacity differences between initial discharge and charge were 42% (CNTs + KB mixture), 43% (commercial Co_3O_4 powder), and 12% (CNTs/Co_3O_4 composite). A low difference indicates that a higher capacity was retained during the initial discharge–charge process. The above results indicate that the composite electrode have a superior reversibility as compared to the rest of materials. However, this improvement is not sufficient for
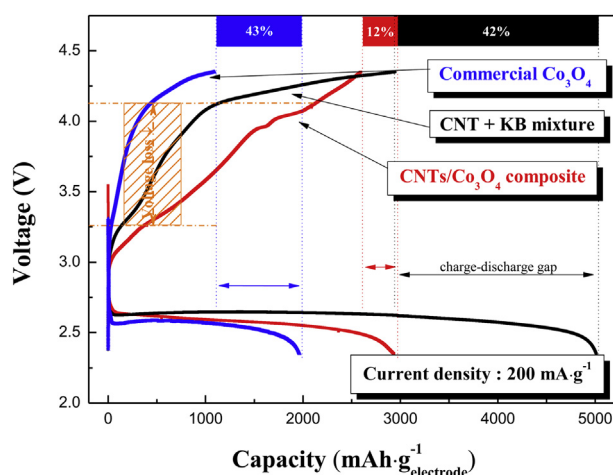
Fig. 8. Comparison of the over-potentials during the initial discharge–charge profiles of the air electrodes (voltage range: 2.35–4.35 V, current density: 200 mA g^{-1}).

"commercial" rechargeable batteries. The rapid capacity loss upon initial cycling may be dominantly attributed to insufficient decomposition of the reaction products formed during the discharging process. It has been previously reported that air electrodes do not fully dissociate the reaction products after a large depth-of-discharge process [11–13]. Consequently, the residual reaction products rapidly decrease the specific capacity after successive cycles. Considering the above theory, a cycling test was performed under a limited discharge capacity of 1000 mAh g$_{electrode}^{-1}$ in order to avoid large depth-of-discharge of the electrodes (discharge voltage was also limited to 2.0 V). The decomposition of the electrolytes at a high voltage range has been also suggested as a possible cause of the capacity loss upon cycling. Thus, the upper cut-off voltage was slightly decreased to 4.2 V, instead, this potential was held until the current density reached 2 mA g^{-1}, which is 1/100 of the current density (200 mA g^{-1}) used for this test to facilitate the decomposition of reaction products. Fig. 9 displays the discharge–charge profiles of the electrodes under the limited capacity and low upper cut-off

voltages (the loading weight of the electrodes was adjusted 1.8 ± 0.1 mg cm^{-2}).

The electrodes containing the CNTs + KB mixture and the commercial Co$_3$O$_4$ powder retained the set-up capacity (1000 mAh g$_{electrode}^{-1}$) only after several cycles, and the discharge voltage significantly decreased afterward (Fig. 9a, b). This may be associated with the loss of catalytic activity of the electrode. In contrast, the electrode containing polydopamine-assisted CNTs/Co$_3$O$_4$ composite showed a largely improved cyclic performance, as shown in Fig. 9c. This implies that the enhanced catalytic activity of the composite not only decreased the over-potential but also improved the cyclic performance behavior. However, after 15 cycles the discharge voltage profile gradually decreased, thereby indicating an increased internal resistance. Fig. 10 presents the cyclic performance of the electrode under a limited capacity (1000 mAh g$_{electrode}^{-1}$). The electrodes retained their set-up discharge capacity (1000 mAh g$_{electrode}^{-1}$) for 16 (composite electrode), 5 (commercial Co$_3$O$_4$), and only 2 cycles (CNTs + KB mixture).

Considering the cycling results, it seems that the CNTs/Co$_3$O$_4$ composite is considerably effective on improvement of cyclic performance of the air electrode. However, it is still not enough for commercial rechargeable battery system. The limitations in cyclic performance are typically associated with side reactions during cycling. To analyze the side reaction and investigate the reaction product on cycling, the constituent elements (C and Li) of the surface of the air electrode were analyzed by secondary ion mass spectrometry (SIMS). Fig. 11a presents the measured points of on cycling and Fig. 11b–e shows the element images of the air electrode containing CNTs/Co$_3$O$_4$ composite obtained by the SIMS analysis. The spot intensity is an indicator of the element-concentration. In the image of the pristine sample before cycling (Fig. 11b), C was observed uniformly on the surface without detecting Li. After initial discharge (Fig. 11c), the considerable amount of Li was detected on the surface of the air electrode due to the formation of reaction products (such as Li$_2$O$_2$). The Li was almost vanished after initial charge (Fig. 11d), which shows that the reaction products are reversibly decomposed on initial charge process. However, it was noticeable that the Li was still detected after 20th charge process, as shown in Fig. 11e. This indicates that
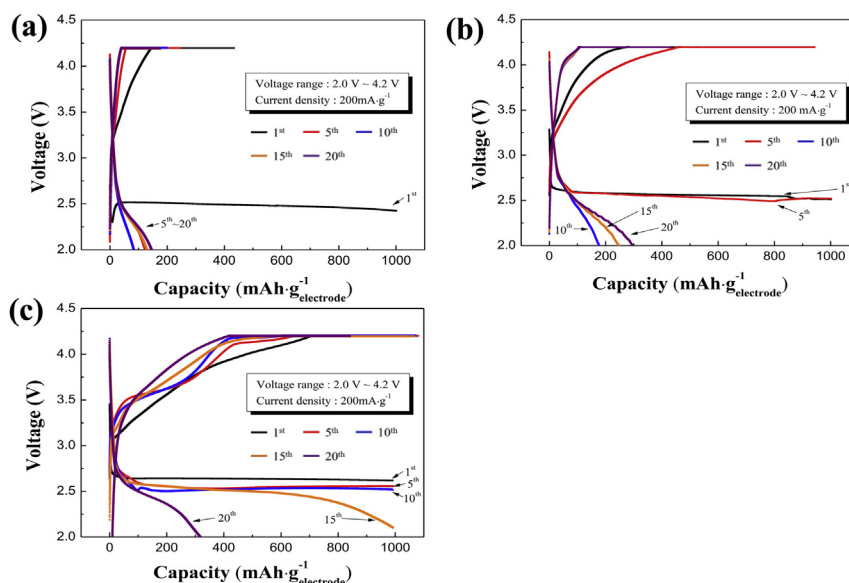

Fig. 9. Discharge–charge profiles of the air electrodes measured under limited capacity (1000 mAh g$_{electrode}^{-1}$) and reduced upper cut-off voltage (4.2 V): (a) Electrode containing CNTs as a catalyst; (b) Electrode containing commercial Co$_3$O$_4$ nanoparticle as a catalyst; (c) Electrode containing polydopamine-assisted CNTs/Co$_3$O$_4$ composite as a catalyst.

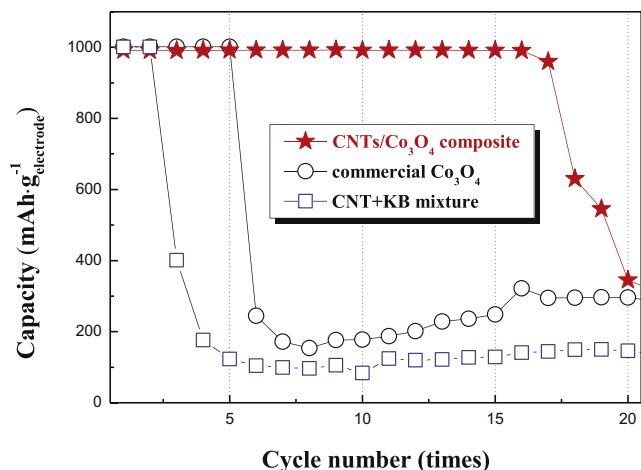**Fig. 10.** Cyclic performance of the air electrodes measured under limited capacity (1000 mAh $g_{electrode}^{-1}$) and reduced upper cut-off voltage (4.2 V).

the reaction products are not clearly removed on charging process but accumulate on the surface of the air electrode.

The phase of the reaction products was examined by HP-XRD analysis of the air electrodes, which were collected at measured points presented in Fig. 11a. The reversibility of the electrochemical process in the Li-air cells is achieved by formation and decomposition of peroxide (Li_2O_2) on cycling. As shown in Fig. 12b and c, it is clearly confirmed that the Li_2O_2 was formed on initial discharge process and decomposed on initial charge process, which is coincident with the previous works using TEGDME-based electrolytes [29–31]. It is noticeable that Li_2CO_3 phase was newly detected at the charged electrode after 20th cycles (Fig. 12d), which implies that the accumulated reaction products, which was observed in Fig. 11e, is associated with Li_2CO_3. As shown in Fig. 12c, the HP-XRD pattern of the initially charged electrode did not presented Li_2CO_3 phase. Li_2CO_3 side-formation has been suggested at the carbon-Li_2O_2 interface after several cycles when operating with TEGDME-based electrolytes [33,34]. So, the residual reaction product, as shown in Fig. 11e, is likely due to the side reactions (such as formation of Li_2CO_3) of the air electrode. This side reaction may lead to
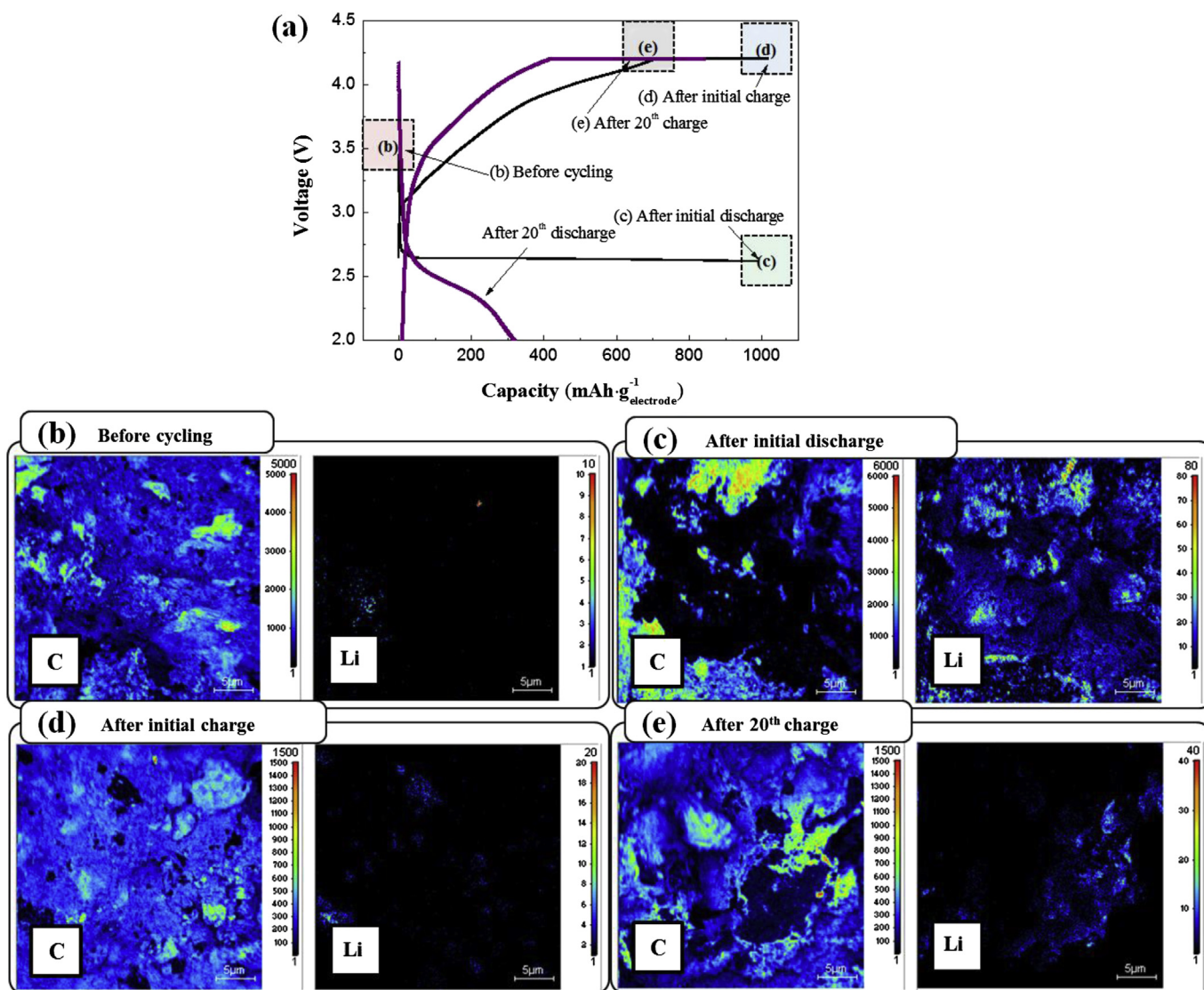

Fig. 11. (a) Measured points of the discharge–charge profile of air electrode containing polydopamine-assisted CNTs/Co_3O_4 composite; element images of the air electrode detected by SIMS analysis: (b) Before cycling; (c) After initial discharge; (d) After initial charge; (e) After 20th charge.
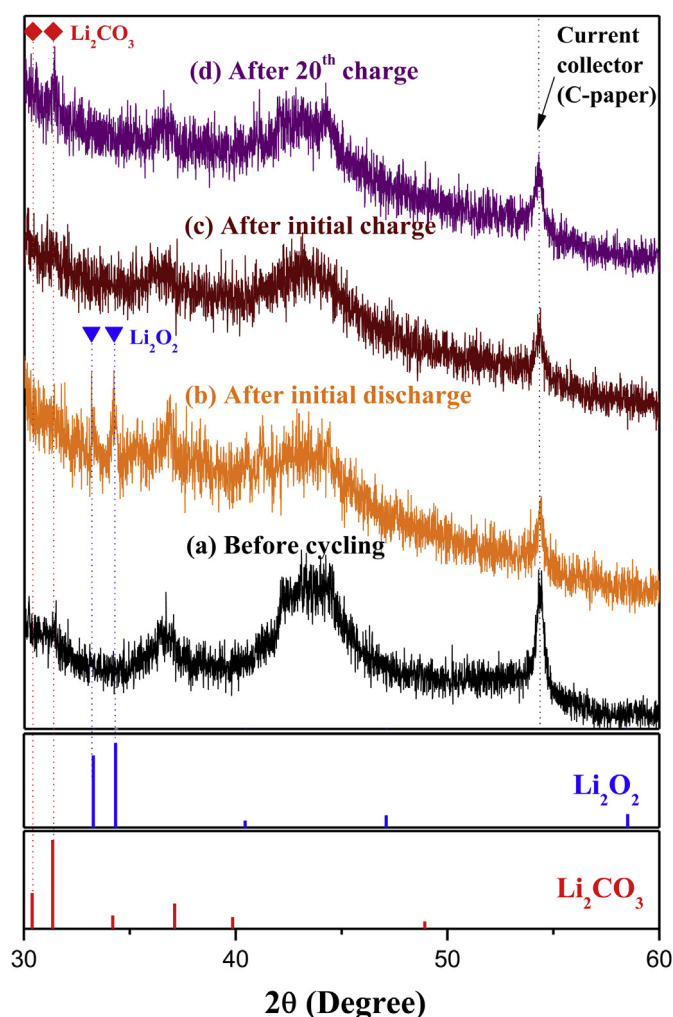
Fig. 12. HP-XRD patterns of air electrode containing polydopamine-assisted CNTs/Co$_3$O$_4$ composite; (a) Before cycling; (b) After initial discharge; (c) After initial charge; (d) After 20th charge.

a gradual decrease in specific capacity during cycling as shown in Figs. 9 and 10. Moreover, the small amount of accumulated Li$_2$O$_2$ due to incomplete decomposition on the air electrode may be also associated with degradation of cycling. In order to enhance the cyclic performance of Li-air batteries, it seemed to be necessary to develop a more stable electrolyte, which can prevent from unwanted side reaction between air electrode and electrolyte.

4. Conclusions

In this article, we report an improved catalytic activity of an electrode containing CNTs/Co$_3$O$_4$ composites. As a new approach, polydopamine layer was introduced as reacting assistant between the CNTs and the oxide catalyst (Co$_3$O$_4$). The polydopamine layer was found to be very effective for the adhesion of nanosized Co$_3$O$_4$ particles on the surface of CNTs, and this is attributed to its hydrophilicity and reactivity with oxide-sources. This beneficial effect of the polydopamine layer allowed the composite to be homogeneously covered with highly dispersed Co$_3$O$_4$ nanoparticles on the

surface of CNTs. The catalytic activity of the electrodes containing polydopamine-assisted CNTs/Co$_3$O$_4$ composites was much higher as compared to those of the electrodes containing the CNTs + KB mixture or commercial Co$_3$O$_4$ nanopowders. The over-potential and cyclic performance of the air electrodes were significantly enhanced by introducing the polydopamine-assisted CNTs/Co$_3$O$_4$ composite as a catalyst. We believe this good behavior of the composite can be explained by the presence of homogeneously dispersed Co$_3$O$_4$ nanoparticles, which may provide a larger catalyst/carbon contact area, thereby enhancing the catalytic activity. Furthermore, the stable contact between the Co$_3$O$_4$ catalyst and CNTs may contribute to reduce the contact resistance and enhance the long-term stability of these materials.

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